농학석사학위논문

나트륨으로 포화된 다공성 매질에서 칼슘 이온의 확산 이동

Diffusive Transport of Calcium Ion in a Sodium-saturated Porous Cation Exchange System

2017년 8월

서울대학교 대학원

농생명공학부 응용생명화학전공

정 재 원

A dissertation for the Degree of Master of Science

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이 논문을 농학석사학위논문으로 제출함

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정 재 원의 석사학위논문으로 인준함

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Abstract

Excess sodium ion (Na^+) adversely affects soil physicochemical properties, such as dispersion of clay particles, low hydraulic conductivity, and soil crusting. Therefore, calcium ion (Ca^{2+}) has been frequently chosen to displace excess Na^+ from the soil profile, since the affinity for exchange sites is greater for Ca^{2+} than for Na^+. In natural systems where CO_2 is ubiquitous, however, Ca^{2+} undergoes precipitation with CO_2 during the diffusion process and the removal of Ca^{2+} from the solution may cause retardation of Ca^{2+} transport and reduce displacement efficiency. One-dimensional diffusive Ca^{2+} transport in a Na^+-saturated porous cation-exchange resin model system was investigated to examine the effect of Ca^{2+} on the removal patterns of Na^+ from the model soil. This study presumes that Ca^{2+} interacts with CO_2 in the presence of H_2O producing $CaCO_3$ and H^+. The production of H^+ and $CaCO_3$ was evidenced by a lowering of pH and by the XRD (X-ray diffraction) analysis, respectively. Each acryl column was packed with a mixture of sand and Na^+-saturated cation-exchange resin was used to dilute the high cation-exchange capacity (CEC) of the resin with sand to a level (10 $cmol_c\ kg^{-1}$) of a typical kaolinitic soil. Four rates of Ca treatment including a control were chosen for comparison (×0, ×0.5, ×1 and ×2 CEC). An equivalent amount of $CaCl_2$ for each treatment was applied on the surface of the mixture in each column simulating one-dimensional diffusion from an instantaneous planar source into a semi-finite system. Retardation of Ca^{2+} transport due to $CaCO_3$ precipitation was characterized by

a lowering of pH of the system, and the advancing front of Ca^{2+} movement in both aqueous and exchanger phases progressed deeper with time. With increasing rates of calcium treatment, diffusion coefficients calculated for Ca^{2+} increased. Therefore, the efficiency of Na^{+} removal from the exchange sites was enhanced as the rate of Ca^{2+} treatment increased. In the soils treated with Ca^{2+} equivalent to ×1 and ×2 CEC, the removal of Na^{+} from the exchanger was effective in respect of the effectiveness of excess Na^{+} removal and the penetration depth of Ca^{2+} dominance. Considering the subsequent resalinization, the application of Ca^{2+} at a rate of ×2 CEC was most effective in the presence of CO_2. As a result, part of our results suggests that at least the application rate of Ca^{2+} should exceed the CEC of a target soil to guarantee efficient removal of Na^{+} from the salt-affected soils

Key Words: Collective diffusion, Desalinization, Diffusion, Snow plow effect, Sodic soil, Sodium-Calcium exchange, transport

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List of Abbreviations

BCSR	Basic Cation Saturation Ratio
CEC	Cation Exchange Capacity
EC	Electrical Conductivity
ESP	Exchangeable Sodium Percentage
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
SAR	Sodium Adsorption Ratio
XRD	X-ray Diffractometry

INTRODUCTION

Salt-affected soils have most often occurred under arid and semiarid climates (Mavi et al., 2012), but nowadays can often be found where the tidal flats were reclaimed along the seacoast. The total area of sodic and saline-sodic soils is estimated at 60 percent of the world's salt-affected soil that covers about 1×10^9 ha (Qadir et al., 2002). Sodic soils are characterized by high exchangeable sodium percentage (ESP), and electrical conductivity (EC) due to the presence of excess levels of sodium (Na) (Kim et al., 2016), adversely affecting soil physicochemical characteristics.

The presence of excess sodium in soils causes dispersion and disintegration of surface aggregates, thus resulting in surface crusting and low hydraulic conductivity (Tang et al., 2006). As a consequence, such unfavorable soil characteristics may inhibit the movement of air and water through the soil, which increases the chances of runoff. Therefore, effective removal of excess sodium from the soil profile is prerequisite to improving soil physicochemical characteristics.

Calcium in soil is effective to prevent soil crusting and improve the structural stability of soil. Reclamation of salt-affected soils can be achieved through a number of different calcium amendment approaches such as either soluble amendments, calcium chloride, gypsum and phosphogypsum or relatively much less soluble amendment, lime. Also, the types of amendment techniques on sodic soil can be classified into three categories. Frist, physical technique, successive or pulse irrigation, leaches out the salt using fresh water or water with amendment application. Second, biological method is

phytoremediation. Extracellular enzyme from plant root dissolves native calcite to provide calcium ion (Ca^{2+}) for exchange complex without the application of an amendment (Zia et al., 2007). Third, chemical approach is the use of chemical amendments by ion exchange reaction.

In case of physical technique, it is not inappropriate to directly apply physical method to wash excess sodium using irrigation with fresh water due to the structural instability of sodic soil (David et al., 2002). Phytoremediation strategy has been found to be too slow to remove excess sodium compared with the efficiency of chemical and physical technique (Qadir et al., 2001). Chemical process, ion exchange reaction, has long been used for their benefits on the reclamation of sodic soil. Calcium has been chosen to leach sodium since selectivity of exchange for calcium is greater than sodium (Brady et al., 2008).

In chemical method, the dosage of calcium amendment has been developed by many researchers over the world to remove excess sodium in soil (Bahçecİ., 2009). The calcium requirement is mostly calculated based on current ESP and final (or target) ESP of the soil together with the consideration of cation exchange capacity (CEC), bulk density, soil depth, etc (Rasouli et al., 2013). In natural systems where carbon dioxide (CO_2) is ubiquitous, however, Ca^{2+} undergoes precipitation with bicarbonate ions (CO_3^{2-}) during the transport process. The removal of Ca^{2+} from the solution may cause retardation of Ca^{2+} transport and reduce displacement efficiency. Also, After the reclamation of sodic soil, resalinization is a general phenomenon. In arid- and semi-arid area, where the amount of evaporation is bigger than rainfall, salts are rapidly accumulated again in the root zone layer of soil (Amin, 2004). In reclaimed land along the shore, where high water table with poor drainage, salts come

easily up to surface due to capillary phenomenon (Jung et al., 1983). So, it is necessary to be investigated for an optical amount of calcium amendment to maintain the continuous state of desalinization and complete reclamation of salt-affected soil.

Recently, much interest has increased in the fate of Ca^{2+} under diffusion process to improve the efficiency of calcium amendment on excess sodium removal in unsaturated conditions. Although there are abundant literatures on the reclamation of sodic soil at existence of both advection and diffusion under a saturated condition, only few studies have been reported on the effects of Ca^{2+} for sodic soil by only diffusion at an unsaturated condition. The effect of factors related to diffusive transport are not generally linear relationship according to water contents (Hu et al., 2003). Also, unlike the existence of both advection and diffusion, there are unique kinetics and equilibrium when Ca^{2+} is transferred by only diffusion in the presence of ubiquitous CO_2. Thus, it is difficult to apply the result of diffusion process investigated in a saturated condition to that in an unsaturated condition.

The fate of Ca^{2+} and the efficiency of calcium amendment in an unsaturated soil can be described several ways. One of the most commonly employed is to study one-dimensional diffusive transport of Ca^{2+}. One-dimensional diffusive Ca^{2+} transport in a Na^{+}-saturated porous cation-exchange resin model system was investigated to examine the effect of Ca^{2+} on the removal patterns of Na^{+} from the model soil and to suggest the application rate of calcium amendment on Ca amendment/soil CEC ratio.

MATERIALS AND METHODS

Preparation of sodium-saturated resin and inert quartz sand

A strongly acidic cation-exchange resin (Amberlite IR-120 Na^+-form, DOW Chemical co, Midland, MI, USA) was chosen for the transport study. The resin has a particle size distribution between 0.6 and 0.8 mm and a cation exchange capacity (CEC) of 430 $cmol_c\ kg^{-1}$. A chemically inert quartz sand (white quartz, Sigma-Aldrich, St. Louis, MO, USA) was used to dilute the high CEC of the resin to a level (10 $cmol_c\ kg^{-1}$) of a typical kaolinitic soil. The Na^+-saturated resin was chosen to simulate the conditions similar to those characterizing sodic soils. Each 20 g of the resin was placed in an Erlenmeyer flask and then shaken with deionized water in 100 mL aliquots at 200 rpm for 10 minutes to remove impurities and excess Na^+ until the $AgNO_3$ test for the Cl^- was negative. This resin was then kept at a moisture content of 0.97 kg kg^{-1} on a dry mass basis. The quartz sand has a particle size distribution between 0.2 and 0.3 mm, and was washed with 1 *M* HCl and subsequently rinsed with deionized water until the $AgNO_3$ test for the Cl^- was negative. This bulk sand was air-dried, and the pH of which was 6.5.

Preparation of cylindrical acryl columns

Each cylindrical acryl column was 50 mm in inner diameter and 110 mm deep, and consisted of 11 interlocking rings, each 10 mm thick. Resin and quartz were mixed to produce a model soil with the CEC of 10 $cmol_c\ kg^{-1}$ such as a typical kaolinite. The cylindrical acrylic columns were packed with model soil at the

bulk density of 1.55 Mg m^{-3}, and the water content was adjusted to 0.06 kg kg^{-1}. The set of packed columns was placed in incubator as an upright position and allowed to pre-incubate at 20 ℃ for 24 h before the application of calcium amendment. Calcium chloride ($CaCl_2$, 95.0 %, Junsei Chmeicals Co., Tokyo, Japan) was used for calcium amendment. There are three levels of treatment in sand and model soil; Calcium amendment / CEC ratio (A) control, (B) ×0.5 CEC, (C) ×1 CEC, (D) ×2 CEC at sand and model soil. An equivalent amount of $CaCl_2$ for each treatment was applied on the surface of the mixture in each column simulating one-dimensional diffusion from an instantaneous planar source into a semi-finite system. After calcium amendments applied, the top of the columns was sealed to prevent evaporation of moisture and placed in incubator for 10 days of incubation period at a constant temperature of 20 ℃. The transport study was experimented in triplicate per treatment.

Column segmentation and physicochemical analysis

After the desired period of incubation, each column was sectioned in 10 mm intervals using a cutter knife. Samples were taken from each section for physical and chemical analysis. Approximately 4 g of soil was used to determine water content (w/w). Other 4 g of samples from each section was weighed for measuring pH and electrical conductivity (EC) using pH and EC meter (Orion 3 star, Thermo Scientific, Pittsburgh, PA, USA). 2g of samples from each section, with a soil/solution ratio of 1:10, was shaken for 60 min at 200 rpm and centrifuged at 3000 rpm for 5 min. the extract solution defined as the water-extractable cation fraction. Following water extraction, the same soil sample was extracted with two successive aliquots of 20 ml of 1 *M* HCl. The

extract solution was termed as the acid-extraction fraction. The water- and acid-extractable faction was referred as the mobile phase and immobile phase, respectively. Both the water- and the acid-extracts were diluted with distilled water to analyze the concentration of cation on each fraction. The sodium and calcium concentration were determined with an inductively coupled plasma-optical emission spectrometer (iCAP™ 7200 ICP-OES, Thermo Scientific, Pittsburgh, PA, USA).

Identification of calcium compound by X-ray diffractometry analysis (XRD)

Air-dried samples for control and ×2 CEC were used to identify the calcium species by the X-ray diffraction technique. Nickel-filtered Cu kα1 at 40kV and 40 mA was used throughout a XRD (D8 Advance, BRUKER, Germany). The samples were step scanned between 5 and 60 degrees.

Cation mass balance

The mass balance of calcium and sodium in each column was calculated as the recovery of cations by the water- and acid-extraction. The sum of both fractions is the amount of total cations per section. The mass of total calcium and sodium was compared with the amount of calcium applied and sodium content in model soil, respectively, which was expressed for a percentage.

RESULTS AND DISCCUSION

The pH profile of model system

The pH profile of control column was approximately 7, which was evenly distributed throughout the column (Fig. 1. A). The distribution patterns of pH were similar from 2 days to 10 days of incubation.

The distribution pattern of pH at various times for the system, ×0.5 CEC, is represented in Fig. 1. B. The pH of the column from surface to 20 mm decreased around 6 and gradually increased to the pH of control columns at 70 mm after 2 days of incubation.

In the columns treated with ×1 CEC, the distribution patterns of pH are illustrated in Fig. 1. C. After 2 days of incubation, the penetration depth of proton (H^+) was 80 mm. The distribution patterns of pH showed that H^+ diffused down to the bottom of the column between 5 days and 10 days of incubation.

In the columns treated with ×2 CEC, the distribution patterns of pH are presented in Fig. 1. D. The concentration of H^+ with ×2 CEC was the highest throughout the column after 10 days of incubation among that with other treatments. Also, the biggest amount of H^+ were diffused downward to the bottom of the column.

The more calcium amendment increased, the more the depth of proton

penetration was deep (Fig. 1. B. C. D). Divalent cations, Ca^{2+} and Mg^{2+}, have superior selective coefficient for exchange site and compete with H^+ on exchange complex (Olatuyi et al., 2009). So, the diffusion rate of H^+ was faster due to cation competition.

pH of the model system decreased below background value with the application of Calcium amendment (Fig.1. B. C. D). The concentration of H^+ was the highest close to the application site and decreased along the distance from the surface of the column. Therefore, there are relationship between the reduction of pH and calcium. The change of pH in the model system was due to the precipitation of calcium carbonate. This reaction is normally accompanied by a rise in proton (Zhang et al., 1997; Xu et al., 2003). In equation (1) and (2), the precipitation of calcium carbonate in porous media under ubiquitous CO_2 is expressed (Jaho et al., 2016)

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + H^+ \quad (1)$$

$$Ca + HCO_3^- \leftrightarrow CaCO_3 \downarrow + H^+ \quad (2)$$

There were two evidences on the precipitation of calcium carbonate. First, calcium carbonate plays a role in the formation of soil aggregates (Enein et al., 2012). Calcium carbonate as cementing agent contributes to the development of soil structure and improves the stability of soil aggregates. In this study, soil consolidation was identified in the column treated with calcium amendment

(Fig. 2). Second, X-ray diffraction (XRD) analysis gave an indication for the crystalline part of calcium carbonate. The XRD analysis showed that the vaterite peak of calcium carbonate precipitated (Fig. 3).

Figure 1. pH profile of columns with various calcium amendment / CEC ratio during incubation.

(A) control, (B) ×0.5 CEC, (C) ×1 CEC, (D) ×2 CEC.

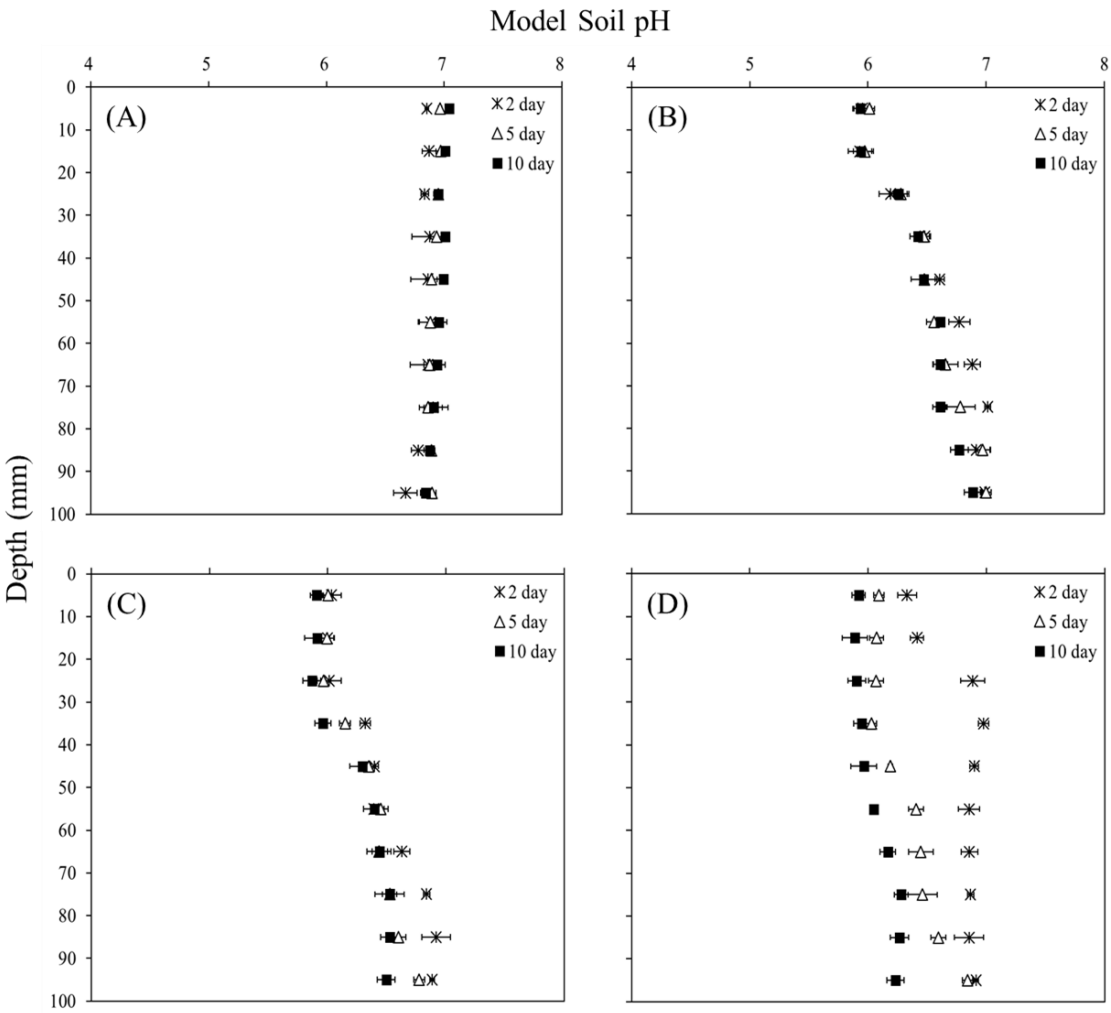

Model Soil pH
Depth (mm)
(A)
(B)
(C)
(D)
2 day
5 day
10 day
4
5
6
7
8
0
10
20
30
40
50
60
70
80
90
100

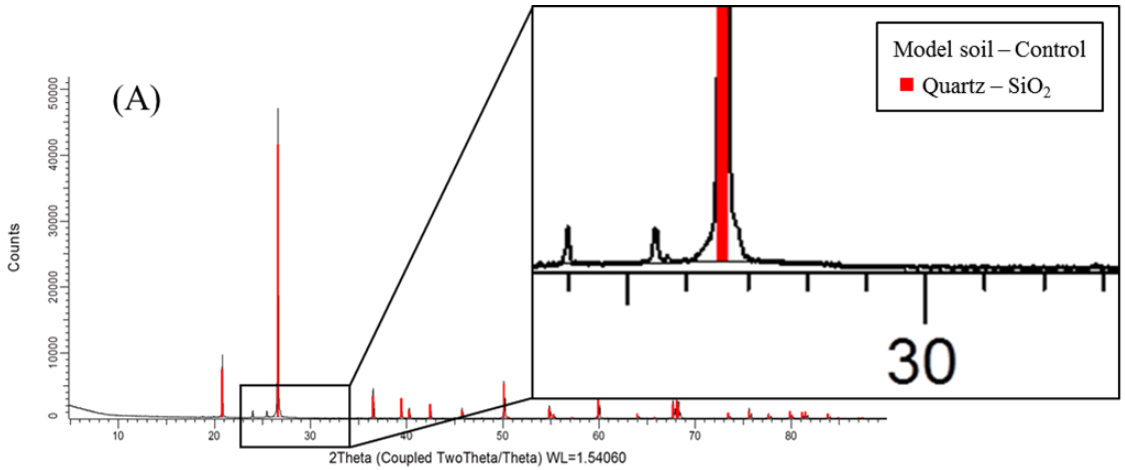
Figure 2. Consolidation phenomenon in sand and model soil.

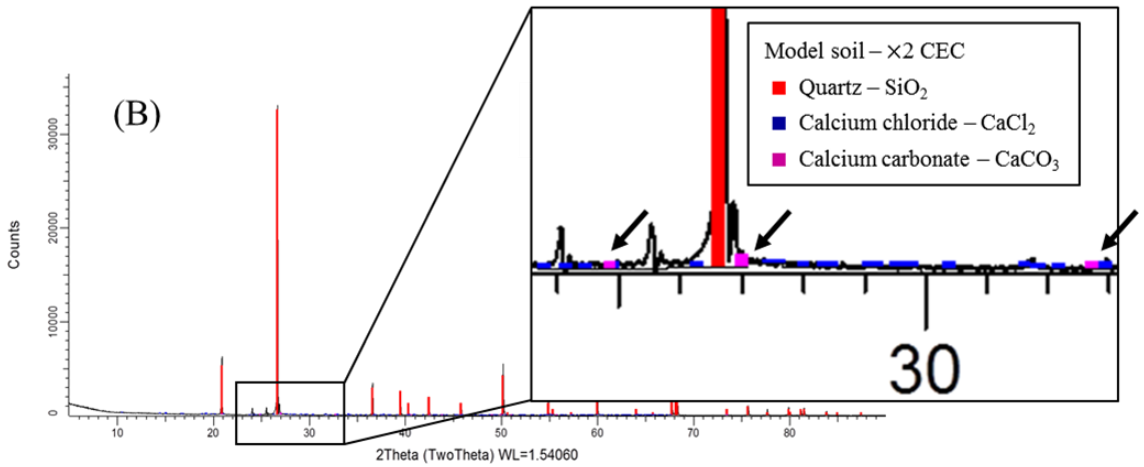
(A) sand and (B) model soil, (a) control and (b) Ca applied.


(A-a)
(A-b)
(B-a)
(B-b)

Figure 3. X-ray diffraction pattern of model soil after 10 day of incubation.

(A) control, (B) ×2 CEC.


(A)
Model soil – Control
Quartz – SiO2
Counts
2Theta (Coupled TwoTheta/Theta) WL=1.54060
30


(B)
Model soil – ×2 CEC
Quartz – SiO2
Calcium chloride – CaCl2
Calcium carbonate – CaCO3
Counts
2Theta (TwoTheta) WL=1.54060
30

Water- and acid- extractable calcium

The water-and acid-extractable calcium distribution profiles in the model system at different time are shown in Fig. 4 and Fig. 5. In the control column, there was no calcium in both water- and acid- fraction (Fig. 4. A and Fig. 5. A). Therefore, calcium was only originated from calcium amendment that we applied.

In the column treated with ×0.5 CEC, the distribution profiles of water-extractable calcium at various times are presented in Fig. 4. B. With time, the concentration of calcium applied on the surface was gradually declined because of diffusion. The distribution patterns are typical one-dimensional diffusive transport. The similar features have been reported by other diffusive transport experiment (Akinremi et al., 1991). Although there was no difference for the advancing front of calcium throughout incubation day, calcium saturation on exchange sites slightly increased during incubation period (Fig. 5. B).

In the columns treated with ×1 CEC, water- and acid-extractable calcium was diffused downward by 50 mm and 90 mm, respectively. (Fig. 4. C and Fig. 5. C). The difference of penetration depth between water fraction and acid fraction was resulted from cation selectivity on exchange site. Calcium, divalent cation, is more like to be adsorbed on exchange sites because cation selectivity increases the higher the charge and the smaller the hydrated radius of the cation (Brady et al., 2008). As a result, calcium was preferentially existed on exchange site, rather than calcium was dissolved in the interstitial solution.

In the column treated with ×2 CEC, water-extractable calcium was transferred at the 70 mm of the column (Fig. 4. D). The depth of calcium-advancing front was the deepest among the treatment. Acid-extractable

Calcium were moved at the bottom of the column between 5 days and 10 days of incubation (Fig. 5. D). The diffusion rate of the column is the fastest among the treatments.

The diffusion coefficients of calcium for each treatment differed. Diffusion coefficient was calculated from calcium distribution in the system after 5 days of incubation. As the amount of calcium amendment increased, the rate of the diffusion coefficient was faster (Fig. 6). When reactive solute such as Ca^{2+} is transferred by diffusion in porous media, effective diffusion coefficient would be changed corresponding to the concentration level of the solute (Malusis et al., 2008). The results indicated that the transport mechanism in the system was not molecular diffusion but collective diffusion. The phenomenon of concentration-dependent diffusion promoted mobility of Ca^{2+} in model system, so Na^{+} was removed rapidly as the increases of calcium amendment.

The mass balance of calcium in water- and acid- extractable fractions on each treatment was carried out (Table 1). The range for mass balance was from 98 % to 103 %. Almost all applied calcium was recovered.

Figure 4. Distribution of water-extractable Ca in the columns with various calcium amendment / CEC ratio during incubation.

(A) control, (B) ×0.5 CEC, (C) ×1 CEC, (D) ×2 CEC.

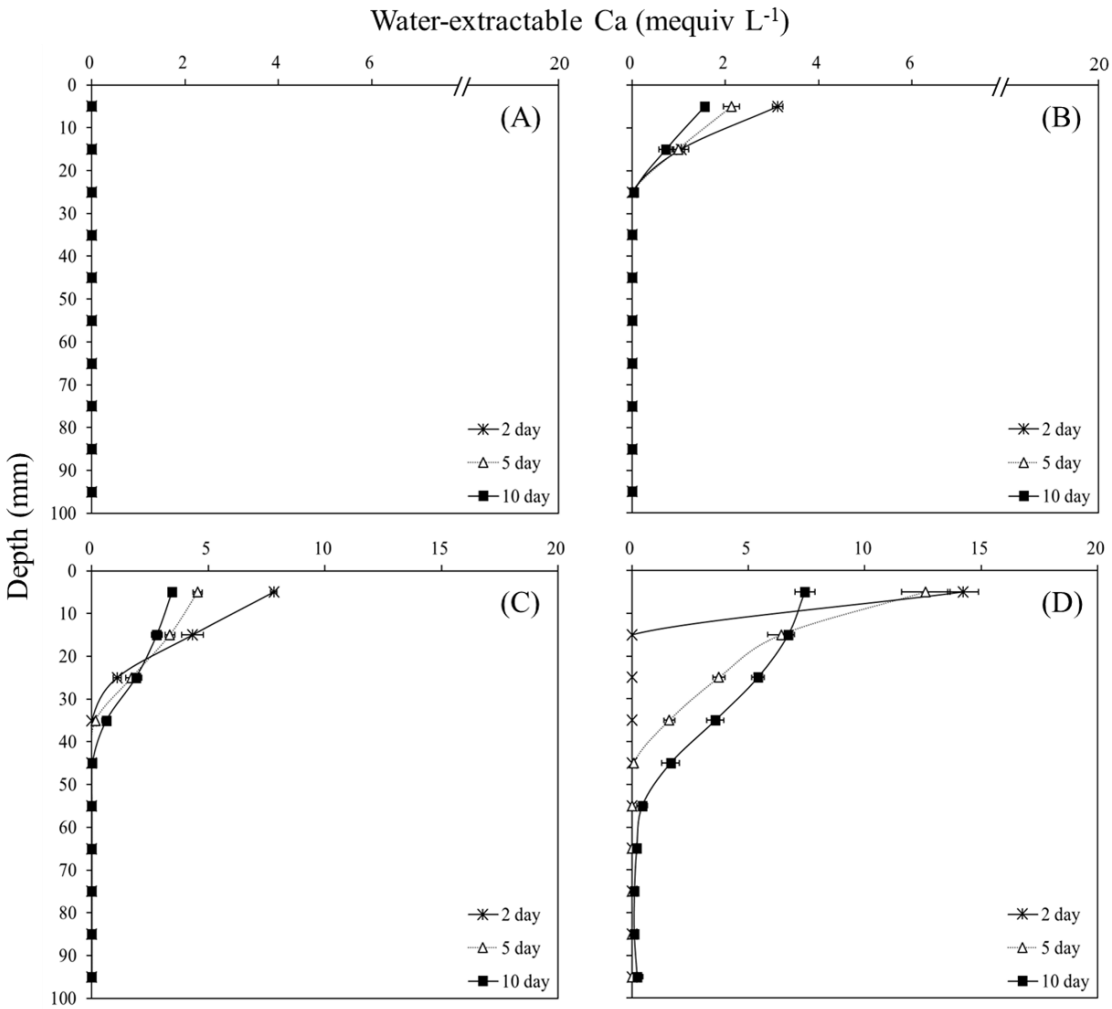

Water-extractable Ca (mequiv L-1)
Depth (mm)
(A)
(B)
(C)
(D)
2 day
5 day
10 day

Figure 5. Distribution of acid-extractable Ca in the columns with various calcium amendment / CEC ratio during incubation.

(A) control, (B) ×0.5 CEC, (C) ×1 CEC, (D) ×2 CEC.

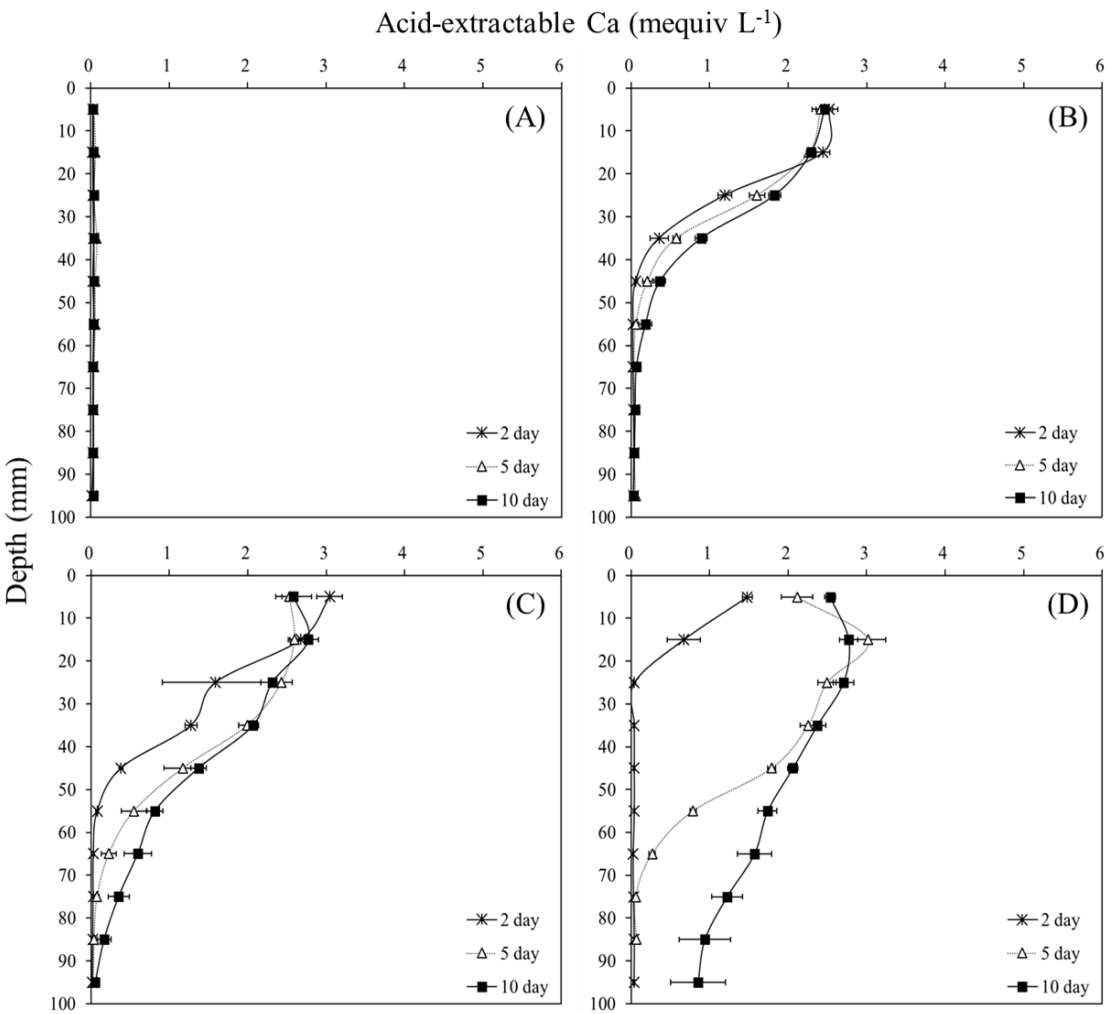
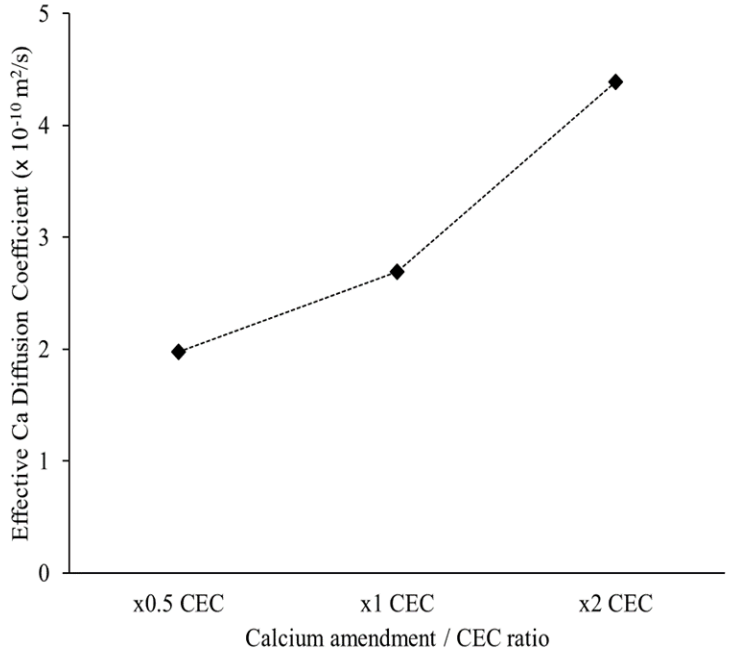

Acid-extractable Ca (mequiv L-1)
Depth (mm)
(A)
(B)
(C)
(D)
2 day
5 day
10 day

Figure 6. Comparison of effective Ca diffusion coefficients after 5 days of incubation.


Effective Ca Diffusion Coefficient (x 10-10 m2/s)
5
4
3
2
1
0
x0.5 CEC
x1 CEC
x2 CEC
Calcium amendment / CEC ratio

Water- and acid- extractable sodium

The distribution patterns of water- and acid-extractable sodium during incubation are presented in Fig. 7 and Fig. 8. The concentration of water-extractable sodium in the control column was zero throughout the column (Fig. 7. A). When calcium amendment was applied on the surface of the columns, however, the amount of sodium in water fraction increased with time due to ion exchange reaction by incoming ion, Ca^{2+} (Fig. 7. B. C. D).

The profiles of acid-extractable sodium in the control column were evenly distributed throughout the column (Fig. 8. A) and kept constant with time. This result indicated that model soil not only was homogeneous peaked into the column, but also was kept stable in a state of sodium-saturated porous media without ion exchange reaction.

In the column treated with ×0.5 CEC, the advancing front of water-extractable sodium is deeper with time (Fig. 7. B). the distribution patterns of acid-extractable sodium were virtually nonexistent at the 0 to 20 mm portion of the column and increased gradually to a concentration of 2 mequiv L^{-1} (Fig. 8. B). Below 50 mm, the amounts of sodium in acid fraction were not altered with time. Therefore, the vertical removal of exchangeable sodium didn't almost happen after 2 days of incubation in this treatment.

In the column treated with ×1 CEC, water-extractable sodium was diffused at the bottom of the column between 5 days and 10 days of incubation (Fig. 8. C). However, acid-extractable sodium gradually increased between 40 mm and 80 mm to the concentration of 2 mequiv L^{-1} that was on the condition of the control column (Fig. 8. C). Also, displacing ion, Ca^{2+}, didn't exist at 100 mm of the column (Fig. 5. C). As a results, water-extractable sodium at the 100 mm

originated in sodium diffused from the upper soil layer.

In the column treated with ×2 CEC, the distribution patterns of water-extractable sodium in the column are represented in Figs. 7. D. After 10 days of incubation, the amount of the water-extractable sodium in the column was the largest among the other treatment. This results indicated that sodium was effectively desorbed from the exchange site, and the concentration of acid-extractable sodium throughout the column is below half compared with that in the control column (Fig. 8. A. D).

In all columns applying calcium amendment, exchangeable sodium on exchange complex was moved into the interstitial solution, which was pushed ahead by the advancing front of calcium (Fig. 4 and Fig. 7). The characteristics of the shape resulted from snow plot effect. The phenomenon of snow plow effect in soil column have been reported in the published literatures (Barry et al., 1983; Starr et al., 1991). As the concentration of incoming solution, Ca, increased, the advancing front was sharper (Fig. 8. B, C, D). The shape for the advancing front was related to selectivity coefficient, the concentration of displacing ion, and the CEC (Cho., 1985). Consequently, the pattern of snow plow effect was another indicator that the efficiency of Na removal was improved as increasing the amount of calcium amendment.

The mass balance for sodium in mobile and immobile phase on each treatment was calculated (Table 1). The range for mass balance is from 100 % to 107 %. Almost all sodium in the artificial system was recovered.

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Figure 7. Distribution of water-extractable Na in the columns with various calcium amendment / CEC ratio during incubation.

(A) control, (B) ×0.5 CEC, (C) ×1 CEC, (D) ×2 CEC.

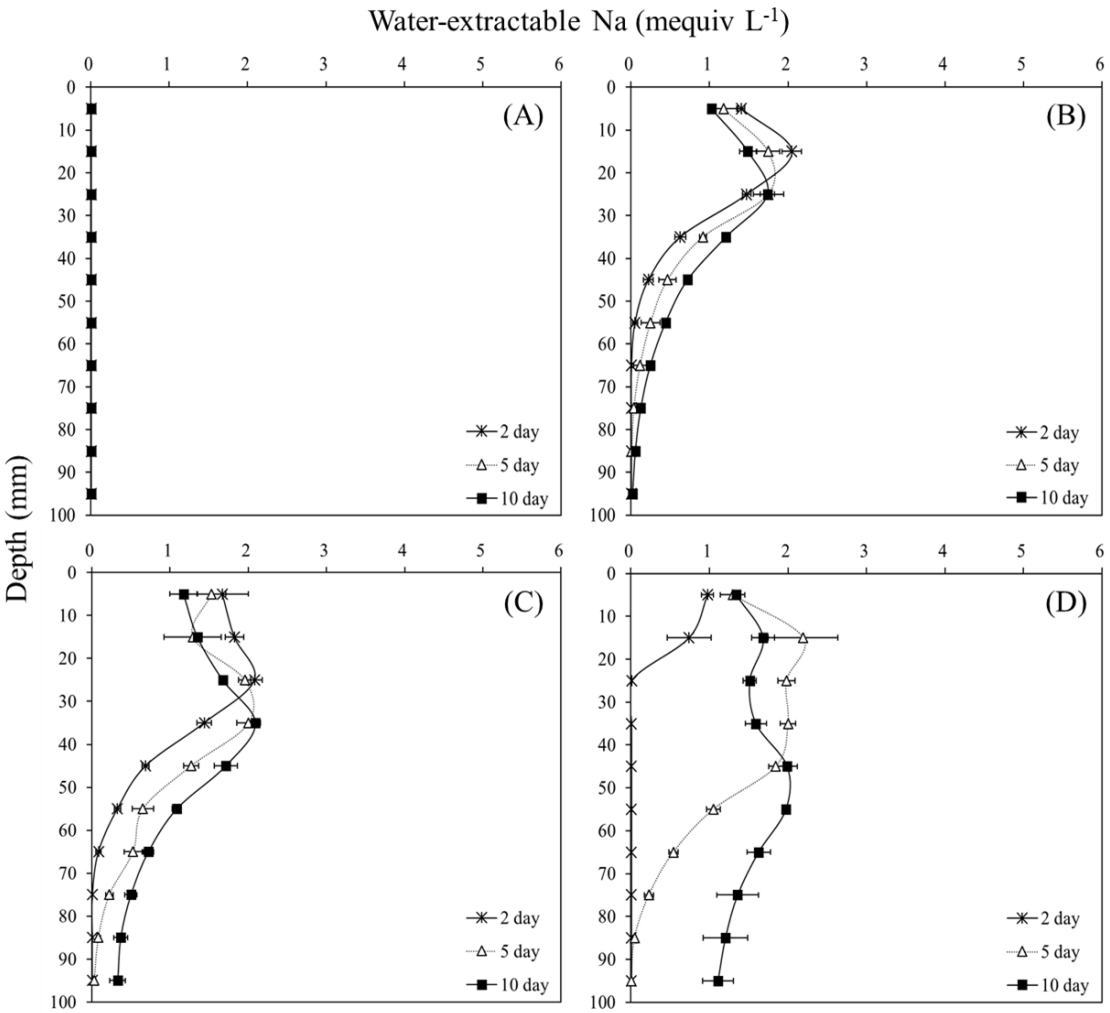

Water-extractable Na (mequiv L-1)
Depth (mm)
(A)
(B)
(C)
(D)
2 day
5 day
10 day

Figure 8. Distribution of acid-extractable Na in the columns with various calcium amendment / CEC ratio during incubation.

(A) control, (B) ×0.5 CEC, (C) ×1 CEC, (D) ×2 CEC.

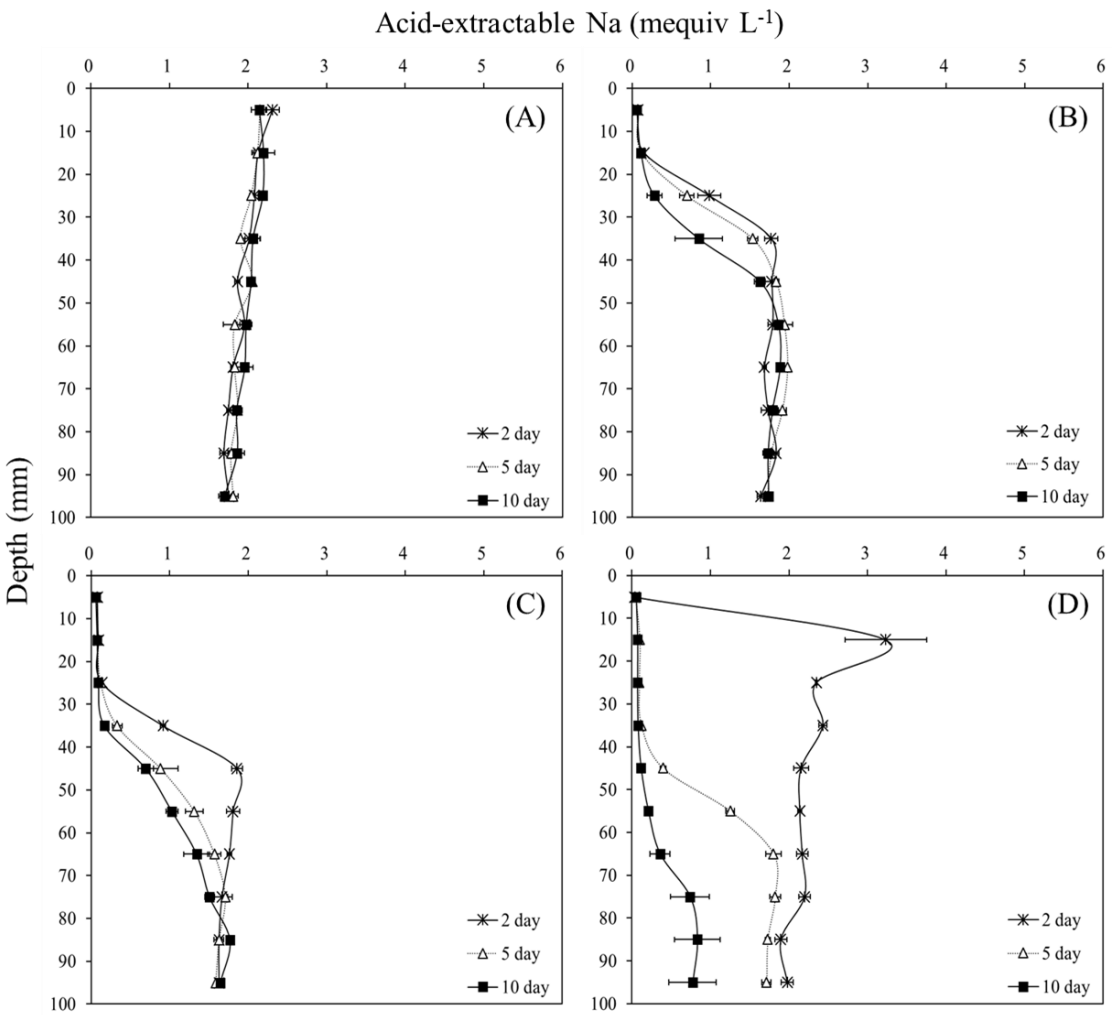

Acid-extractable Na (mequiv L-1)
Depth (mm)
(A)
(B)
(C)
(D)
2 day
5 day
10 day

Table 1. Mass balance of Na and Ca calculated from ICP analysis for various Ca treatments on model soil.

Ca applied/CEC ratio	Incubation day	Total extractable Na	Total extractable Ca	Na in model soil	Input Ca	Mass balance	
						Na	Ca
		g				%	
Control	2 day	0.73 (0.01)		0.7		104	
	5 day	0.74 (0.01)		0.7		106	
	10 day	0.73 (0.03)		0.7		104	
× 0.5 CEC	2 day	0.72 (0.01)	0.31 (0.00)	0.7	0.31	103	100
	5 day	0.75 (0.00)	0.31 (0.00)	0.7	0.31	107	100
	10 day	0.7(0.01)	0.31 (0.00)	0.7	0.31	100	100
× 1 CEC	2 day	0.73 (0.02)	0.6 (0.01)	0.7	0.61	104	98
	5 day	0.71 (0.02)	0.63 (0.01)	0.7	0.61	101	103
	10 day	0.73 (0.01)	0.62 (0.01)	0.7	0.61	104	102
× 2 CEC	2 day	0.74 (0.01)	1.2 (0.03)	0.7	1.22	106	98
	5 day	0.74 (0.01)	1.2 (0.01)	0.7	1.22	106	98
	10 day	0.73 (0.01)	1.21 (0.01)	0.7	1.22	104	99

Mean values with standard deviations in parentheses

The quantitative evaluation of sodium removal

There are several concepts to evaluate the reclamation of sodic soil. According to the traditional method, The ESP of 10-15 % is generally accepted as a critical level to prevent adverse effects of sodium in soil (Güler et al., 2014). In the column treated with ×2 CEC, the ESP was only close to the threshold value (Fig. 9).

In contrast to the traditional method, the reclamation of sodic soil can be accessed by calcium saturation on exchange site. First, according to basic cation saturation ratio (BCSR) known as mineral balancing (Eckert, 1987), 65 to 85% calcium of Soil CEC is optimal range to allow maximum growth of plant and improving soil physical and chemical properties. Second, Rural Development Administration (RDA) has found that upland-field crops generally grow the best when the range of exchangeable calcium is approximately from 50 % to 60 % (NIAST, 2010). On the basis of the above criteria, the amount of sodium removed in the column with ×1 CEC and ×2 CEC was appropriate (Fig. 9).

It is also important to access the extent of desalinization with depth. In this study, 65 % calcium saturation of soil CEC was defined as Ca dominance in accordance with BCSR. Below 65 % calcium saturation was defined as Na dominance. The distribution profiles of Ca dominance at various treatment during incubation are shown in Fig. 10.

In the column treated with ×0.5 CEC, the depth of calcium dominance is 30 mm (Fig. 10. B). The depth was not altered after 5 days of incubation. The efficiency of vertical reclamation was low. In the column treated with ×1 CEC, although the advancing front of Ca was 90 mm (Fig. 5. C), the depth of Ca dominance was 50 mm (Fig. 10. C). Therefore, both the amount of excess

sodium removed and the depth of Ca dominance should be considered for the assessment on reclamation of sodic soil. As a result, in this column, the significant level of desalinization was about 50 %. In the column treated with ×2 CEC, Ca dominance sharply increased by 80 mm during incubation. The efficiency of vertical reclamation was the best among the treatments.

The completion of soil reclamation should be accomplished by both lowering target ESP and declining potential risk of resalinization. One of the reasons on resalinization is the high concentration of sodium in mobile phase because this phenomenon is attribute to the process of equilibrium between mobile and immobile phase of soil. Sodium adsorption ratio (SAR) was used to represent water-soluble solute content in mobile phase.

Sodium adsorption ratio (SAR) is expressed by eq. (3)

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{\frac{\mathrm{Ca}^{2+}+\mathrm{Mg}^{2+}}{2}}} \qquad (3)$$

Sodium adsorption ratio (SAR) is important index to estimate the exchangeable sodium in soil. The relationship between ESP and SAR is positive (Laurenson et al., 2011). To ensure effective sodium removal over the long term, SAR should be maintained the low level. If SAR is high value, the soil layer has a potential and/or long-term risk of secondary soil salinization. As a result, it is necessary to manage both exchangeable cation content and water-solute cation content for completion of reclamation process. In this study, SAR will be used as an indicator for accessing potential risk of resalinization and completing the reclamation of sodic soil.

In the column treated with ×0.5 CEC, the peaks and distribution patterns of SAR maintained constant shape with time. The results represented that the high level of sodium in water-soluble content was constant with time. So, desorbed sodium back diffused to exchange complex. In the column treated with ×1 CEC, the peak of SAR was moved downward during incubation. However, both the area of SAR and Potential risk of resalinization below 50 mm increased. In the column treated with ×2 CEC, the peak of SAR was not only lowered but also changed to flat shape. So, there was scarcely the potential risk of resalinization.

Figure 9. Exchangeable cation saturation percentage on exchange complex after 10 days of incubation.

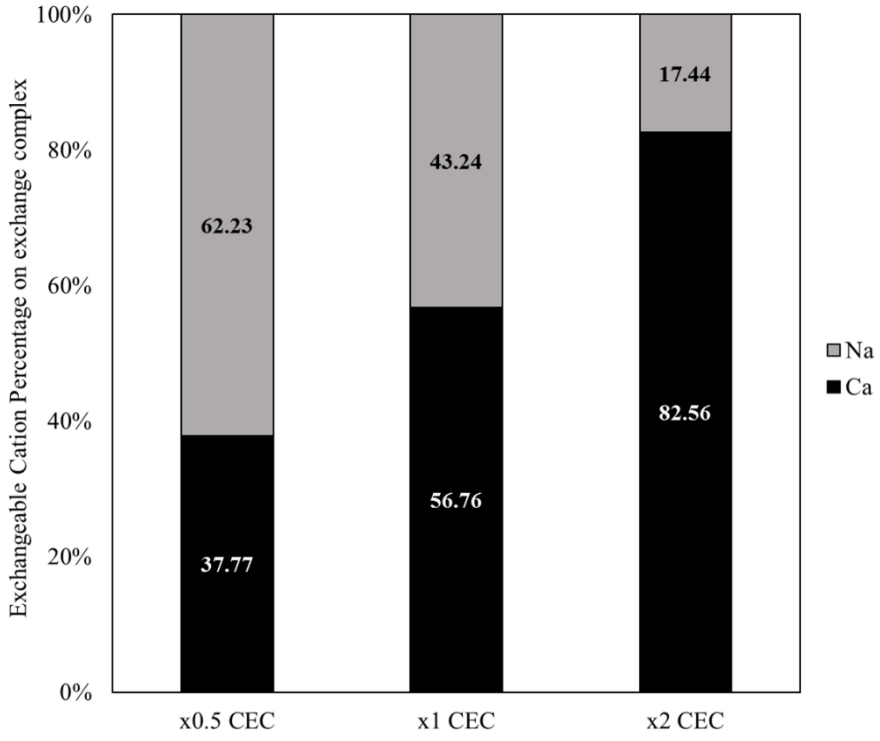

100%
80%
60%
40%
20%
0%
Exchangeable Cation Percentage on exchange complex
62.23
37.77
43.24
56.76
17.44
82.56
x0.5 CEC
x1 CEC
x2 CEC
Na
Ca

Figure 10. Profile of Ca- and Na- dominance in the columns with various calcium amendment / CEC ratio during incubation.

(A) control, (B) ×0.5 CEC, (C) ×1 CEC, (D) ×2 CEC.

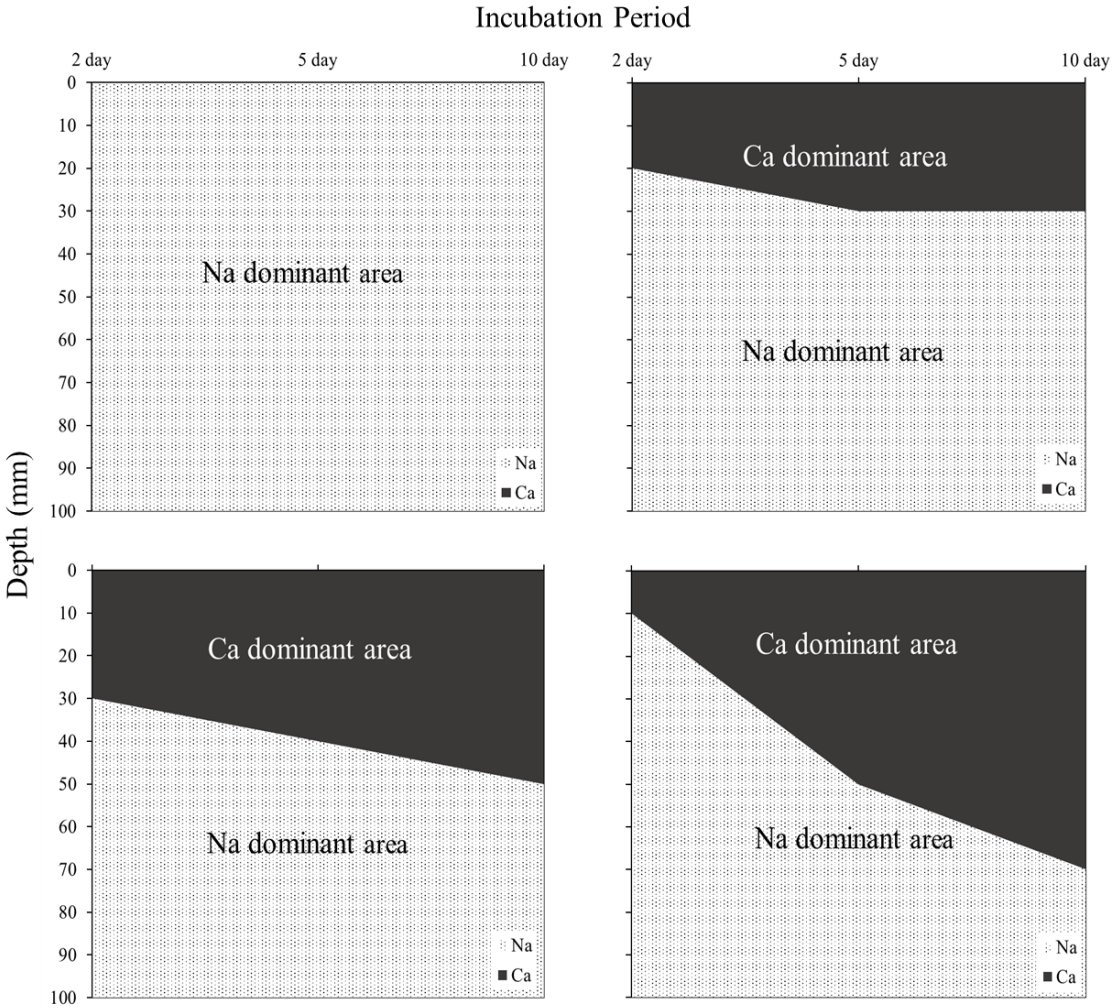
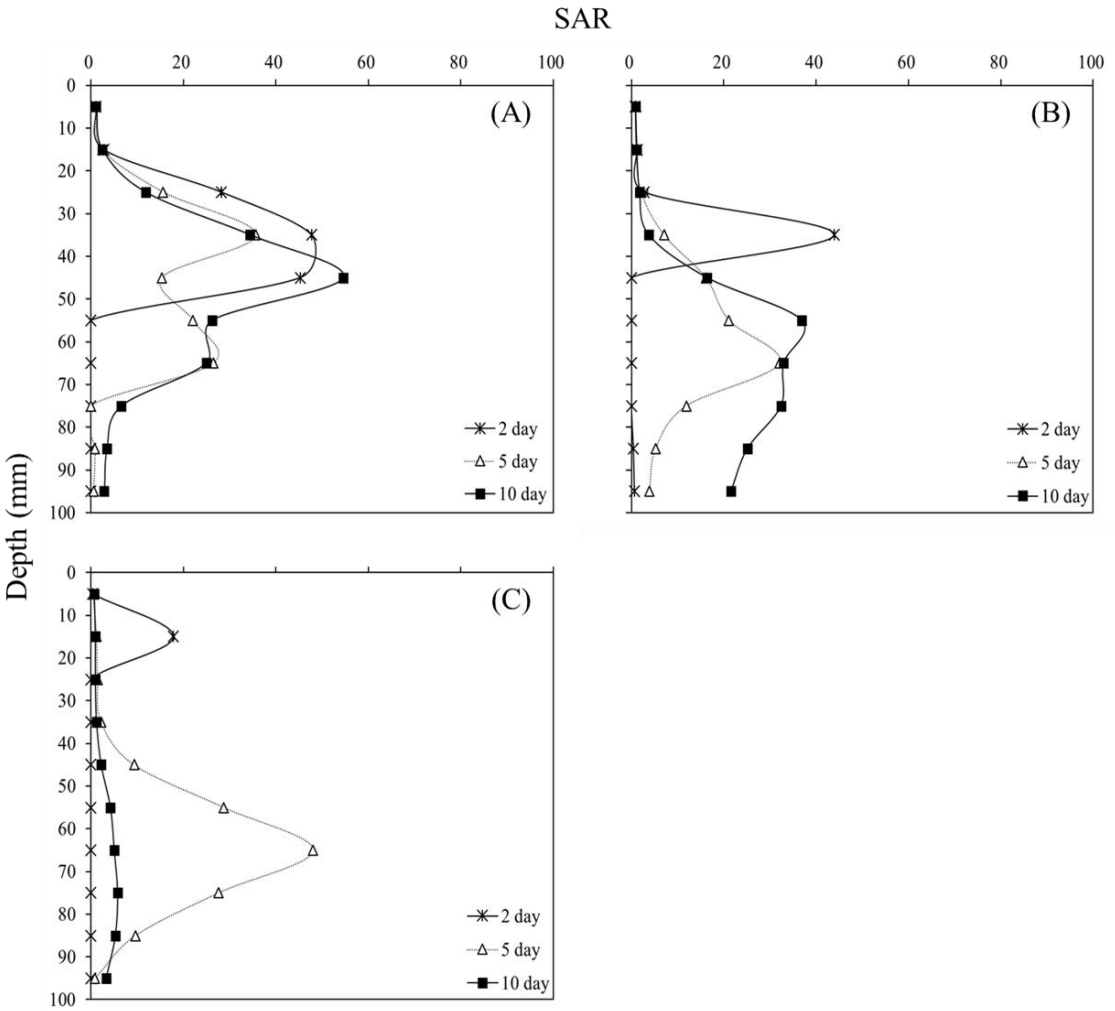

Incubation Period
2 day
5 day
10 day
Depth (mm)
0
10
20
30
40
50
60
70
80
90
100
Na dominant area
Ca dominant area
Na
Ca

Figure 11. Distribution of SAR in the columns with various calcium amendment / CEC ratio during incubation.

(A) ×0.5 CEC, (B) ×1 CEC, (C) ×2 CEC.


SAR
Depth (mm)
(A)
(B)
(C)
2 day
5 day
10 day

CONCOLUSION

This study was conducted to examine the effect of exchangeable Ca^{2+} on the removal patterns of Na^{+} from the model soil and to suggest the application rate of calcium amendment on Ca amendment/soil CEC ratio. The pH of the model system decreased below background value with the application of calcium amendment. XRD analysis gave an indicator for the crystalline part of calcium carbonate. The precipitation of calcium carbonate was one reason on reducing sodium removal. The diffusion coefficients of calcium for each treatment differed. Diffusion coefficients calculated for Ca^{2+} is faster with increasing rates of calcium treatment. Therefore, the efficiency of Na^{+} removal from the exchange sites was enhanced as the rate of Ca^{2+} treatment increased. In all columns applied calcium amendment, exchangeable sodium on exchange sites was moved into the interstitial solution, which was pushed ahead by the advancing front of calcium. The characteristics of the shape resulted from snow plot effect. As the concentration of incoming solution, Ca^{2+}, increased, the advancing front was sharper. Consequently, the pattern of snow plow effect is another indicator that the efficiency of sodium removal was improved with increasing the amount of calcium amendment. Completion of soil reclamation should accomplish both lowering target ESP and declining potential risk of resalinization. In the column treated with ×2 CEC, the peak of SAR was only altered as flat form after 10 days of incubation. Unlike other treatment, there was scarcely the potential risk of resalinization in the column with ×2 CEC. As a result, when calculating the dose of calcium amendment, we take into

consideration to compensate for the loss of the precipitation reaction and potential risk of resalinization. The experimental results suggested that calcium amendment must be applied over the soil CEC to leach effectively away excess sodium from exchange sites.

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Abstract in Korean

토양 내 과량의 나트륨은 점토를 분산시키고, 수리전도도를 감소시키며, 토양 피각을 형성하여 토양 물리화학성에 악영향을 미친다. 칼슘 이온은 나트륨 이온보다 토양 교환체에 대한 친화도가 높기 때문에 토층 내 과량의 나트륨을 제거할 때 칼슘이 이용된다. 그러나 자연계에는 이산화탄소가 존재하여 칼슘은 확산 이동 과정에서 이산화탄소와 침전 반응을 일으킨다. 침전에 의한 토양수 내 칼슘 이온 감소는 칼슘 이동을 지연시키고 양이온 교환 효율을 떨어뜨린다. 나트륨으로 포화된 다공성 양이온 교환 수지 모델 시스템에서 칼슘의 1차원 확산 이동은 모델 토양에 존재하는 나트륨의 제거 양상에 대한 칼슘 이온의 효과를 조사하기 위해 실험되었다. 이 연구는 물에 녹은 이산화탄소와 칼슘이 반응하여 탄산칼슘과 수소 이온이 형성된다고 가정하였다. 수소 이온과 탄산칼슘 생성은 산도 감소와 XRD 분석 결과로 확인 되었다. 모래와 나트륨으로 포화된 이온교환수지 혼합물을 각각의 아크릴 컬럼에 채웠으며, 나트륨으로 포화된 이온 교환 수지는 높은 양이온 교환 능력을 가지고 있어 모래를 이용해 일반적인 카올리나이트 토양 양이온 교환 능력인 10 $cmol_c$ kg^{-1}으로 희석하였다. 무처리구를 포함하여 4 수준으로 칼슘 제제를 처리하여 처리별 칼슘 제제 효과를 비교하였다 (×0, ×0.5, ×1 그리고 ×2 CEC). 각 처리 수준에 해당하는 염화칼슘 당량을 컬럼의 표면에 평면 시용 하였는데 이것은 칼슘이 평면 시용 부분으로부터 1차원 확산 이동하여 반무한 시스템으로 들어가는 것을 가정한다. 탄산칼슘 침전으로 인한 칼슘 이동 지연은 시스템의 산도 감소가 특징이며, 시간이 지남에 따라 토양수와 교환체 표면 모두에서 칼슘 이온의 전선이 점점 깊어졌다. 칼슘 제제

처리량이 증가함에 따라 칼슘 이온의 확산이동계수가 증가했다. 그러므로, 칼슘 제제 처리량이 증가할수록 교환체로부터 나트륨 제거 효율이 향상되었다. 과량의 나트륨 제거 효과와 칼슘 우점지역의 침투 깊이를 고려하면 ×1 CEC 그리고 ×2 CEC 처리구의 토양 내 나트륨 제거가 효과적이었다. 차후 재염화를 고려하면, 이산화탄소가 존재하는 환경에서 칼슘제제를 CEC 대비 2배 처리한 처리구에서 가장 효과적이었다. 결론적으로 우리는 토양의 양이온 교환능력보다 많은 양의 칼슘 제제를 처리해야 효율적으로 과량의 나트륨 제거를 보장할 수 있었다.

주요어 : 나트륨-칼슘 교환, 나트륨성 토양, 분자 확산, 재염, 제염, 집합적 확산, 이동.

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